The potential for a hydrogen water-plasma laser

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A stationary, electronically-excited, population inversion of atomic hydrogen, H, has been observed in a low-pressure water-vapor microwave discharge plasma. The inverted H population was evident from the relative intensities of the transitions within the Lyman series (n = 2, 3, 4, and 5 to n = 1) and within the Balmer series (n = 3, 4, 5, 6, 7, and 8 to n = 2). Lines of the Balmer series of n = 5, and 6 to n = 2 and the Paschen series of n = 5 to n = 3 were of particular importance because of the potential to design blue and 1.3 micron infrared lasers, respectively, which are ideal for many communications and microelectronics applications. High-power hydrogen gas lasers are anticipated at wavelengths, over a broad spectral range from far infrared to violet which may be miniaturized to micron dimensions. Such a hydrogen laser represents the first new gas laser in over a decade, and it may prove to be the most versatile and useful of all.

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For the last fifteen years there has been an aggressive search for a blue laser. A blue laser would significantly improve the performance of many applications and open new venues. Blue lasers that are durable and bright have significant applications such as superior displays, optical sensors, laser printers and scanners, fiber optical and undersea optical communications, medical devices, and higher density compact disk (CD) players. The shorter (blue) wavelength could be more sharply focused such that the capacity of magnetic and optical storage may be increased. Digital versatile disks (DVDs) which rely on red aluminum indium gallium phosphide (AlInGaP) semiconductor lasers have a data capacity of about 4.7 gigabytes (Gbytes) compared to 0.65 for compact discs. The capacity could be increased to 15 Gbytes with a suitable violet laser. Despite the tremendous value of a blue laser, advancements have been limited due to a lack of materials which emit blue light or blue-emitting plasmas capable of lasing.

Recombination of injected electrons and holes in InGaN has been extensively pursued as a suitable blue laser.[1] Unfortunately, after over a decade of effort, blue diode lasers are still plagued by inadequate substrates, crystal layer dislocations, and defects that increase over time with the requisite high-drive currents. Frustration over these and other impediments to commercialization of this important device has given rise to the view that commercial success may depend on the discovery of something completely new.[2]

Inverted Lyman and Balmer populations may permit a continuous wave (cw) laser at blue wavelengths. For the last four decades, scientists from academia and industry have been searching for lasers using hydrogen plasma.[3-6] Developed sources that provide a usefully intense hydrogen plasma are high-powered lasers, arcs and high-voltage DC and RF discharges, synchrotron devices, inductively coupled plasma generators, and magnetically confined plasmas. However, the generation of population inversion is very

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difficult. Recombining expanding plasma jets formed by methods such as arcs or pulsed discharges is considered one of the most promising methods of realizing an H I laser.

Because the population of hydrogen states is overwhelmingly dominated by the ground state even in the most intense plasmas, the realization of an H I laser requires an overpopulation in a state with $n_i > 2$ which decays to a state with $1 < n < n_i$. Thus, an H I laser based on a Balmer transition is feasible for a mechanism which produces an overpopulation in a corresponding state. The Balmer α, β, γ, and δ lines of atomic hydrogen at 6562.8 Å, 4861.3 Å, 4340.5 Å, 4101.7 Å in the visible region are due to the transitions from $n = 3$, $n = 4$, $n = 5$, and $n = 6$ to $n = 2$, respectively. An H overpopulation of $n > 3$ that is above threshold could be the basis of a blue laser. But, lasing of a blue Balmer line has been difficult to achieve even with cold recombining plasmas. Akatsuka and Suzuki,[6] for example, were able to achieve an overpopulation for level pairs 4–3 and 5–4 only for a recombining plasma generated in a arc-heated magnetically trapped expanding plasma jet.[6]

Rather than using recombining arcs or recombining electron-hole pairs in semiconductors to achieve lasing at blue wavelengths, a chemical approach was pursued. It was previously reported that a new chemically generated plasma source has been developed that operates by incandescently heating a hydrogen dissociator and a catalyst to provide atomic hydrogen and gaseous catalyst, respectively, which react to produce an energetic plasma called a resonance transfer (rt)-plasma.[7,8] Intense VUV emission was observed at low temperatures (e.g. $\approx 10^3$ K) and an extraordinary low field strength of about 1–2 V/cm from atomic hydrogen and certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic

hydrogen, $E_h = 27.2\ eV$ where E_h is one hartree. The theory has been given previously.[9,10]

For oxygen, there are several chemical reactions that fulfill the catalyst criterion—a chemical or physical process with an enthalpy change equal to an integer multiple of E_h. The reactions $O_2 \rightarrow O + O^{2+}$, $O_2 \rightarrow O + O^{3+}$, and $2O \rightarrow 2O^+$ provide a net enthalpy of about 2, 4, and 2 times E_h, respectively.[11] Lasing directly from oxygen is unknown, but lasing from inverted water vibration-rotational levels in water plasmas which may be from hydrogen-oxygen mixtures has been achieved several decades earlier.[12] In addition, helium-water plasmas as well as water plasma lasers were explored for a source of submillimeter wavelengths.[13] More recently, emission from $OH^{\bullet}$ radicals in water and helium-hydrogen water plasmas has been investigated as an efficient source of radiation in the region $\lambda < 2000$ Å for the replacement of expensive working media based on krypton and xenon in microelectronics, photochemistry, and medical applications.[14] These prior water-plasma light sources were based on high-voltage glow discharges.

A high-voltage glow discharge water vapor plasma was characterized by absolute intensity measurements of the Balmer lines by fiber optically coupling the plasma emission to a high resolution visible spectrometer (± 0.06 Å) as described previously.[15] As shown in Figure 1a, we observed the known intensity ratios of the Balmer lines. Similarly, no inversion was observed with RF driven water plasmas maintained with experimental setups and conditions reported previously.[15] We had shown previously that the conditions of the particular discharge may be a major parameter in the observation of excessive Doppler Balmer line broadening with plasmas of hydrogen and a noble ion having an ionization potential of an integer multiple of E_h.[8,9,15–17] We proposed that the

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corresponding energetic hydrogen formed with an Evenson microwave cavity may be a means to achieve population inversion.

A microwave water plasma was used as a source of O_2 and atomic hydrogen. Water vapor was formed in a heated insulated reservoir and flowed through a half inch diameter quartz tube at a flow rate of 10 standard $cm^3 \cdot s^{-1}$ (sccm) at a corresponding pressure of 50-100 mtorr. At this pressure, room temperature was sufficient for maintaining the water vapor. The tube was fitted with an Evenson coaxial microwave cavity. The input power to the plasma at 2.45 GHz was set at 50 W and 90 W as described previously.[15] The high resolution visible spectra recorded as described previously[15] with a 50 W or 90 W input is shown in Figure 1b, the population of the level $n = 4$, $n = 5$, and $n = 6$ of hydrogen was continuously inverted with respect to $n = 3$ in the water plasma; whereas, the hydrogen alone spectrum was unexceptional. Similarly, the relative intensities of the Balmer lines of microwave plasmas of hydrogen (90-2%) mixed with xenon, krypton, or nitrogen at 50 W were equivalent those of hydrogen alone; thus, the inversion is not inherent to a hydrogen plasma generated by microwaves. As shown in Figure 1b, when the input power was increased to 90 W, the $n = 5$ and $n = 6$ levels were further continuously inverted with respect to $n = 4$. Thus, wavelength tuneability may be achieved by varying the microwave power with lasing between the corresponding power-dependent inverted levels.

Other explanations of the overpopulation were ruled out. The spectrometer response was determined to be approximately flat in the 4000-7000 Å region by ion etching and with an intensity calibrated lamp. Furthermore, the Balmer and Lyman line intensity ratios of the control hydrogen plasmas closely matched those obtained using the

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NIST Einstein A coefficients.[18] Since these ratios did not change as the pressure was lowered, and the hydrogen pressure was lower in the water plasma than the control, the NIST Einstein A coefficients were used to calculate the number density ratios from the water plasma emission. The water plasma was determined to be optically thin for water absorption of hydrogen Balmer and Lyman lines; thus, absorption of 6562.8 Å and 4861.3 Å and 1215.67 Å emission by $n = 2$ and $n = 1$ state atomic hydrogen, respectively, may be neglected as the cause of the inverted ratios. The absorption cross section of Balmer emission by water is insignificant.[19] Thus, the Balmer lines were used to determine the lasing conditions except for the $n = 2$ level which was determined from the intensities of the Lyman lines. Using the absorption cross section of water for Lyman α emission of $\sigma = 1.6 \times 10^{-17}$ cm^2,[20] the water plasma was determined to be optically thin by the method given previously[16] since the water number density, $N_{H_2O} = 2.5 \times 10^{15}$ cm^{-3}, was low, and the path length, 5 cm, was short.

The absolute reduced Balmer population density of the excited hydrogen atoms $\dfrac{N_n}{g_n}$ with principal quantum numbers $n = 1$ to 9 were obtained from N, their absolute intensity integrated over the visible spectral peaks corrected by their Einstein coefficients, divided by g, the statistical weight ($g = 2n^2$), as discussed by Akatsuka et al.[6] For example, $\dfrac{N_n}{g_n}$ for quantum number $n = 3,4,5,6$ recorded on a water microwave plasma at 90 W input was determined to be 3.44×10^8 cm^{-3}, 9.02×10^8 cm^{-3}, 385×10^8 cm^{-3}, and 116×10^8 cm^{-3} respectively.

To determine the population of the $n = 2$ level, VUV spectra ($900 - 1300$ Å) were recorded on light emitted from water and hydrogen microwave discharge plasmas at

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90 W input power according to methods reported previously.[8] As shown in Figure 1c, the Lyman series was also inverted. From the number densities of the levels determined from the absolute Balmer line intensities and the Lyman lines intensities shown in Figure 1c it was found that

$$\frac{N_4}{N_3} \text{Balmer} = 4.66; \ \frac{N_4}{N_3} \text{Lyman} = 4.46$$

Since $\frac{N_4}{N_3}$ determined from the Lyman series and the Balmer series were about the same, and the Balmer α line was absolutely measured, the absolute number density for $n = 2$ was determined from the absolute Balmer α line intensity.

$$(N_2)_{\text{Balmer}} = (N_3)_{\text{Balmer}} \times \left(\frac{(N_2)\text{Lyman}}{(N_3)\text{Lyman}}\right)$$

Using $N_3 = 6.20 \times 10^9 \text{ cm}^{-3}$ and $g_2 = 8$, $\frac{N_2}{g_2}$ was determined to be $1.74 \times 10^8 \text{ cm}^{-3}$.

With appropriate cavity length and mirror reflection coefficient, cw laser oscillations may be obtained between states having an overpopulation ratio determined by $\frac{N_i}{N_f} \frac{g_f}{g_i} > 1$ where i represents the quantum number of the initial state and f represents that of the final state.[6] On this basis, it was determined that lasing is possible over a wide range from far infrared to violet wavelengths. Representative transitions and wavelengths are shown in Table I. The important parameter for lasing is that the reduced overpopulation density is above threshold. Using standard laser cavity equations,[6] it was determined that the threshold condition is achievable with micron to submillimeter laser cavities for several transitions emitted from these plasmas. For plasma properties of this experiment determined using a Langmuir probe as described previously[21] ($T_e = 2.0 \text{ eV}$,

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electron density $n_e = 0.2 \times 10^8 \text{ cm}^{-3}$), conditions for lasing at 12,818.1 Å, 4340.5 Å, and

4101.7 Å corresponding to the transitions $5 \rightarrow 3$, $5 \rightarrow 2$, and $6 \rightarrow 2$, respectively, were

determined assuming a cavity length of 100 cm and a combined mirror reflection

coefficient of 0.99. The overpopulation ratios $\dfrac{N_5}{N_3}\dfrac{g_3}{g_5}$, $\dfrac{N_5}{N_2}\dfrac{g_2}{g_5}$, and $\dfrac{N_6}{N_2}\dfrac{g_2}{g_6}$ were 112, 221,

and 67, respectively. Threshold reduced $n = 5$ overpopulation densities of about

$0.49 \times 10^7 \text{ cm}^{-3}$ and $4.6 \times 10^7 \text{ cm}^{-3}$ are required for lasing to $n = 3$ and $n = 2$,

respectively, and, a corresponding threshold reduced $n = 6$ overpopulation density of

$6.9 \times 10^7 \text{ cm}^{-3}$ is required for lasing to $n = 2$. The actual reduced overpopulation

densities were much greater, $3.8 \times 10^{10} \text{ cm}^{-3}$, $3.8 \times 10^{10} \text{ cm}^{-3}$, and $1.2 \times 10^{10} \text{ cm}^{-3}$,

respectively. Thus, lasing is expected with cavity lengths of 0.01 cm, 0.2 cm, and 0.6 cm,

respectively.

Lasing is possible at blue wavelengths which are ideal for many communications

and microelectronics applications as well as at a wavelength of 1.3 μm which is ideal for

transmission through glass optical fibers. The emission wavelength of the potential water

laser is about 400 nm which is suitable for the next generation 15-Gbyte DVDs.[1]

Currently, the ideal laser diode for telecommunications applications is the

$In_x Ga_{1-x} As_y P_{1-y}$ diode laser wherein a lattice constant mismatch requires that the laser be

separate from the silicon circuits. An integrated laser would revolutionize

telecommunications, electronics, and computing.[22] Conceptually, we see no obvious

impediment to integration of a water-plasma laser. In addition, many more laser

wavelengths corresponding to Balmer, Paschen, and Brackett lines are possible. With the

capability of lasing over the widest range of atomic wavelengths of any known atomic

laser, far infrared to violet, the hydrogen laser based on water-plasma may prove to be the

most versatile laser yet discovered.

References

[1] S. Nakamura, *Science* **281**, 956 (1998).

[2] R. W. Hardin, "Challenges remain for blue diode lasers" (OE Reports, SPIE 192, December 1999; http://www.spie.org/web/oer/december/dec99/cover1.html).

[3] L. I. Gudzenko, L. A. Shelepin, *Sov. Phys. JETP* **18**, 998 (1963).

[4] S. Suckewer, H. Fishman, *J. Appl. Phys.* **51**, 1922 (1980).

[5] W. T. Silfvast, O. R. Wood, *J. Opt. Soc. Am. B* **4**, 609 (1987).

[6] H. Akatsuka, M. Suzuki, *Phys. Rev. E* **49**, 1534 (1994).

[7] R. Mills, J. Dong, Y. Lu, *Int. J. Hydrogen Energy* **25**, 919 (2000).

[8] R. Mills and M. Nansteel, P. Ray, *IEEE Trans. Plasma Sci.* **30** (2), in press (2002).

[9] R. L. Mills, P. Ray, B. Dhandapani, M. Nansteel, X. Chen, J. He, *J. Quant. Spectros. Radiat. Transfer*, in press (2002).

[10] R. Mills, P. Ray, *J. Mol. Struc.* , in press (2002).

[11] D. R. Linde, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, ed 79, 1998–1999), p. 9.55 and p. 10.175.

[12] A. Crocker, H. A. Gebbie, M. F. Kimmitt, L. E. S. Mathias, *Nature* **201**, 250 (1964).

[13] W. J. Sarjeant, Z. Kucerovsky, E. Brannen, *Appl. Opt.* **11**, 735 (1972).

[14] A. K. Shuaibov, A. I. Dashchenko, I. V. Shevera, *Quant. Electron.* **31**, 547 (2001).

[15] R. L. Mills, P. Ray, E. Dayalan, B. Dhandapani, J. He, *IEEE Trans. Plasma Science*, (To be published).

[16] R. L. Mills, P. Ray, *New J. Phys.* **4**, 22.1 (2002).

[17] R. L. Mills, P. Ray, B. Dhandapani, J. He, *J. Appl. Phys.*, (To be published, MS#JR02-0987.

[18] NIST Atomic Spectra Database, www.physics.nist.gov/cgi-bin/AtData/display.ksh.

[19] J. G. Calvert, J. N. Pitts, *Photochemistry* (Wiley, New York, 1966), pp. 200–202.

[20] R. K. Vatsa, H. R. Volpp, *Chem. Phys. Lett.* **340**, 289 (2001)..

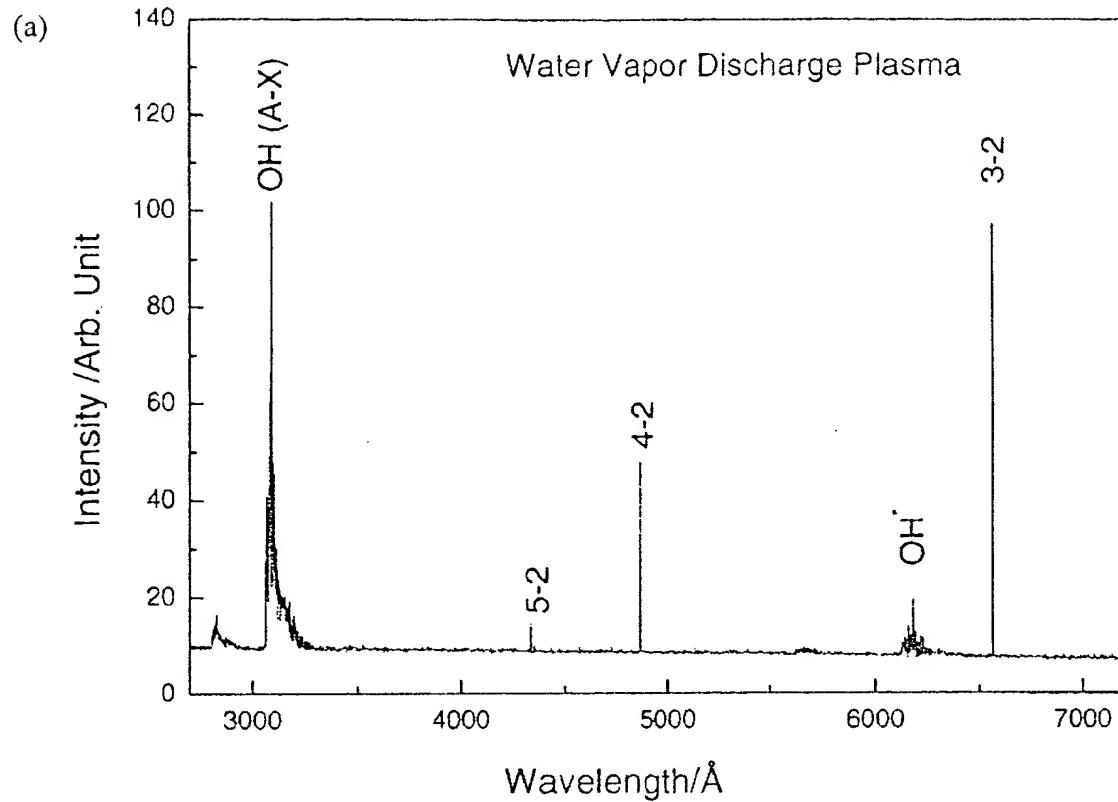[21] D. Barton, J. W. Bradley, D. A. Steele, and R. D. Short, *J. Phys. Chem. B* **103**, 4423 (1999).

[22] P. Ball, *Nature* **409**, 974 (2001).

Table I.   Potential laser transitions of atomic hydrogen in a microwave water-vapor
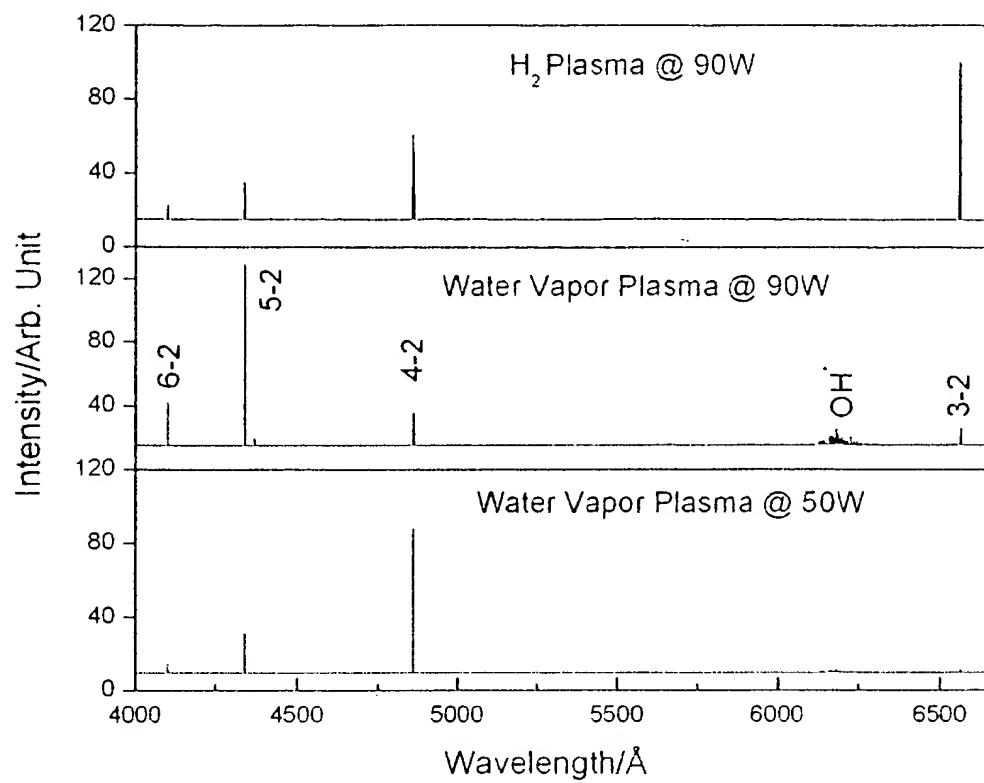
plasma.

wavelength/Å	spectral region	electronic transition $n_{initial} - n_{final}$
74,578	IR	$6 \rightarrow 5$
40,512	IR	$5 \rightarrow 4$
26,252	IR	$6 \rightarrow 4$
18,751	IR	$4 \rightarrow 3$
12,818	IR	$5 \rightarrow 3$
10,938	IR	$6 \rightarrow 3$
10,049	IR	$7 \rightarrow 3$
6,563	red	$3 \rightarrow 2$
4,861	blue	$4 \rightarrow 2$
4,340	violet	$5 \rightarrow 2$
4,102	violet	$6 \rightarrow 2$
3,970	violet	$7 \rightarrow 2$
3,889	violet	$8 \rightarrow 2$

Figure Captions

Figure 1. Water vapor and hydrogen plasma spectroscopy. (a) The visible spectra (3000-7000 Å) of the cell emission from a water glow discharge microwave plasma with 90 W input power. No Balmer line inversion was observed. (b) The visible spectra (4000-6700 Å) of the cell emission from a hydrogen microwave plasma at 90 W input power (top), a water microwave plasma with 90 W input power (middle), and a water microwave-plasma with 50 W input power (bottom). Stationary inverted H Balmer populations were observed from the low-pressure water-vapor microwave discharge plasmas. The population of the level $n = 4,5$, and 6 of hydrogen was continuously inverted with respect to $n = 3$ at 50 W and at 90 W input power to the water plasma; whereas, when the input power was increased to 90 W, the $n = 5$ and 6 levels were further continuously inverted with respect to $n = 4$. (c) The VUV spectra (900 – 1300 Å) of the cell emission from hydrogen microwave (dotted line) and the water microwave (solid line) plasmas with 90 W input power. An inverted Lyman population was observed from the water plasma emission with the inversion observed in the visible as shown in Figure 1b extending to the $n = 2$ level.

(a)

Water Vapor Discharge Plasma

Intensity /Arb. Unit vs Wavelength/Å

OH (A-X), 5-2, 4-2, OH·, 3-2

(b)

Intensity/Arb. Unit

H$_2$ Plasma @ 90W

Water Vapor Plasma @ 90W

6-2

5-2

4-2

OH

3-2

Water Vapor Plasma @ 50W

Wavelength/Å

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(c) Water Vapor Plasma @ 90W

Photon Counts/Sec vs Wavelength/Å

Peaks labeled: 5-1, 4-1, OH, 3-1, m-H₂, m-H₂, m-H₂, m-H₂, m-H₂, m-H₂, m-H₂, m-H₂, m-H₂, 2-1, H₂ Plasma